Journal of International Scientific Publications:
Materials, Methods & Technologies, Volume 7, Part 1
ISSN 1313-2539, Published at: http://www.scientific-publications.net

NANOPOROUS CERAMIC HYBRID MATERIALS SYNTHESIZED BY ORGANICALLY MODIFIED CERAMIC PRECURSOR WITH TERMINAL AMINE GROUP

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Abstract

Nanoporous ceramic materials was functionalized by co-condensation of tetraethyl orthosilicate (TEOS) and different 3-aminopropyltriethoxysilane (APTES) amounts in the presence of amphiphilic triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) ($EO_{20}PO_{70}EO_{20}$), who was previously dissolved in acid solution with different acid concentrations. Pluronic P123 was used as structure-directing agent and xylene as a swelling agent. Inorganic salt was introduced in order to improve structure ordering and to tailor framework porosity. The synthesized materials were characterized by scanning electron microscopy (SEM), X-ray diffraction, nuclear magnetic resonance (^{29}Si MAS NMR and ^{13}C CP MAS NMR), Fourier –transform infrared spectroscopy (FT-IR) and elemental analysis. The results from NMR and FT-IR show that the organic functional group is successfuly incorporated in the silica framework and P123 was successfully extracted. The results from all analyzes prove that the acid concentration has significant influence on the materials morphology and properties.

Kay words: *sol-gel, mesoporous materials, hybrid materials, as structure-directing agent.*

1 INTRODUCTION

In the last 20 years, the demand for materials with specific physico-chemical properties is increasing (Díaz et al, 2009). Organic-inorganic hybrid porous materials are currently attracting particular interest because they combine the advantages of inorganic and organic components (Dabrowski et al,2007). Organic-inorganic hybrid porous materials are prepared under mild conditions by sol-gel polycondensation of tetraalkoxysilane $Si(OR)_4$ and appropriate silane coupling agent R` Si(OR)3 organotrialkoxysilane, were R` represents a ligand containing functional group, which greatly expands the area of application of these materials (Shea & Loy 2001, Saadeh & El-Ashgar 2006). These materials are called 'hybrids' since the inorganic and organic parts are completely homogeneously mixed at the molecular scale within the whole sample (Hoffmann & Fröba, 2011). The sol-gel route has attracted much attention in materials science due to its unique advantages, such as the low temperature process, high homogeneity of the final products and the capability to create materials with controlled surface properties and a wide range of pores (Dabrowski et al, 2007). The main properties featured by these Organic-inorganic hybrid materials are highly ordered structures and uniform pore size distributions within a framework formed by a homogeneous distribution of organic and inorganic moieties (Shang-Ru et al, 2008). The homogenous distribution of organic groups has significant influence on the surface properties, reactivity and accessibility of the final porous materials (Goto &

Inagaki, 2002). Other factors, such as starting materials (e.g., alkoxides, metal salts etc, surfactants as structure directing agent), reaction parameters (e.g. pH, temperature, solvent, co-solvent etc.) also influence the formation of porous structures and dictate the pore size, its distribution and ordering (Naik & Ghosh 2009, Wahab et al. 2004). Integration of amine functional groups into the structure of mesoporous organic-inorganic silica hybrids is of big interest due to the versatile applications of the resultant materials provided by the chemistry of the amine functional group, which include base-catalysis [14] coupling and immobilization of functional molecules and biomolecules [15], drug delivery [16], adsorption and sequestration of heavy metal ions (Wang et al. 2005, Lei et al. 2002, Munoz et al. 2003, Walcarius et al. 2003, Lui et al. 2000).

In this paper we report on synthesis of porous amine functionalized organosilicas prepared via a sol-gel process by using a co-condensation of aminefunctionalized trialkoxysilane (3-aminopropyltriethoxysilane (APTES)) and tetraethylortosilacate (TEOS) in the presence of nonionic surfactants in acid ambient. The samples were synthesized with different APTES amount in HCl solution with different concentration. The final hybrid materials were characterized by XRD, solid-state ^{29}Si MAS NMR, ^{13}C CP MAS NMR, FT-IR, SEM and elemental analysis.

2 EXPERIMENTAL

2.1 Chemicals

Tetraethyl orthosilicate (TEOS, MERCK) and (3-aminopropyl)triethoxysilane (APTES, Aldrich) were used in order to synthesize the amine-functionalized porous gels. Triblock copolymer Pluronic P123 $PEO_{20}PPO_{70}PEO_{20}$, (Sigma-Aldrich, Mn~5,800) was used as a structure directing agent. Xylene (Aldrich) was used as a swelling agent. To improve the structure ordering and tailor framework porosity was used KCl (Aldrich). Hydrochloric acid (HCl, 36%, Promark Chemicals), Ethanol (99.8%) and distilled water were used for removal of surfactant P123.

2.2 Synthesis

In a typical synthesis, 1.2g P123 and 3.5g KCl were dissolved in 52 ml 1M, 2M or 0.18M HCl and 10 ml distilled water at room temperature. 2.64 ml xylene was added after dissolving of KCl and P123. After 1 hour stirring with xylene TEOS was added. The solution was stirred for 1 hour at room temperature and APTES was added (drop-by- drop) at continuous stirring (Figure 1). The chemical composition of the samples is presented in Table 1. The obtained materials were dried at 100°C for 24 hours.

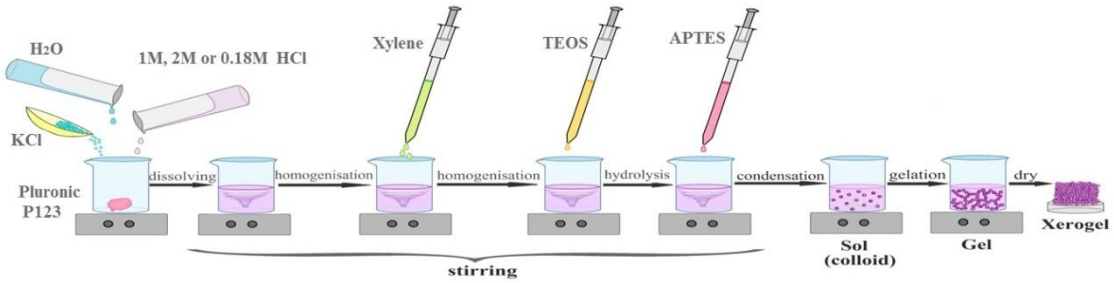

Figure 1 Scheme of synthesis of the samples

Table 1. Chemical composition of the samples

Sample	P123 [g]	KCl [g]	H_2O [ml]	HCl Molar concentration	HCl 2.0, 1.0 or 0.18 M [ml]	Xylene [ml]	TEOS [ml]	APTES [ml]
NSI 1	1.2	3.5	10	2.0 M	52	2.64	2.64	2.71
NSI 2	1.2	3.5	10	1.0M	52	2.64	2.64	2.71
NSI 3	1.2	3.5	10	2.0M	52	2.64	2.64	4.06
NSI 4	1.2	3.5	10	1.0M	52	2.64	2.64	4.06
NSI 5	1.2	3.5	10	0.18M	52	2.64	2.64	4.06
NSI 6	1.2	3.5	10	2.0M	52	2.64	1.24	2.71
NSI 7	1.2	3.5	10	1.0M	52	2.64	1.24	2.71

2.3 Surfactant extraction

The removing of the surfactant was performed by soaking of the synthesized hybrid materials in solution of ethanol and hydrochloric acid (Figure 2): 1gr from the sample was soaked in 150ml ethanol and 1.7ml 36% HCl at 50°C for 24 hours. The resulting solids was collected by filtration, washed with distilled water and ethanol, and dried at 50°C for 24 hours.

Figure 2. *Extraction of P123*

2.4 Materials characterization

Powder X-ray diffraction patterns were obtained on a Rigaku/ New X-Ray Diffractometer System "Geigetflex" D/Max- C Series), working with Cu-Kα radiation with a range of 0.4-5.0 (2θ), and scanning speed 0.01° 2θ/min. The morphology of the samples was observed by scanning electron microscopy (SEM) the images were recorded on a Hitachi S-4100 scanning electron microscope with an acceleration voltage of 15 kV. ^{13}C (100.61MHz) cross-polarization magic angle spinning (CP MAS) and ^{29}Si (79.49 MHz) MAS solid-state NMR experiments were recorded on a (9.4 T) Bruker Avance 400 spectrometer. The experimental parameters for ^{13}C CP MAS NMR experiments: 9 kHz spin rate, 5 s pulse delay, for ^{29}Si MAS NMR experiments: 5 kHz spin rate, 60s pulse delay. MAS

NMR spectra were measured with 40 μs 1H 90º pulse, speed of rotation 50 kHz. ^{29}Si solid-state NMR spectra were recorded at 79.49 MHz on a (9.4 T) Bruker Avance 400 spectrometer ^{29}Si magic angle spinning MAS NMR spectra were measured with 40 μs 1H 90º pulse, speed of rotation 50 kHz and a delay of 60 seconds. Fourier transform infrared (FT-IR) measurements were performed on a MATTSON 7000 Spectrometer in the range 4000–400 cm-1 and resolution 2 cm^{-1} The FT-IR spectra were recorded at room temperature using KBr pellets, 32 scans were signal averaged. FT-IR was used to confirm the removal of surfactants and the formation of organosilica materials. Elemental analyses for C, N and H were performed with a Truspec 630-200-200 elemental analyzer at combustion furnace temperature 1075^{o}C.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the XRD patterns of all samples after surfactant extraction. XRD patterns reveal only one diffraction peak in the low angel diffraction region (from 1 to 5 o) at about 2Theta=1.15^{o}. This single peak indicates the characteristics 2-D hexagonal mesostructure (Hao et al. 2011) of ordered materials (Wang et al. 2005, Urata et al. 2011, Katiyar et al. 2006, Wahab et al. 2004, Hao et al. 2011). The absence of higher angle refractions in Figure 3 suggests the lack of long-range order (Wang et al. 2005, Huaqin et al. 2009). All samples show the same diffraction peak with similar intensity values and on the base of these results we can conclude that the concentration of HCl and the ratio (TEOS+APTES)/ (P123+HOH+KCl+xM HCl), has not significant influence on the morphology of the final materials.

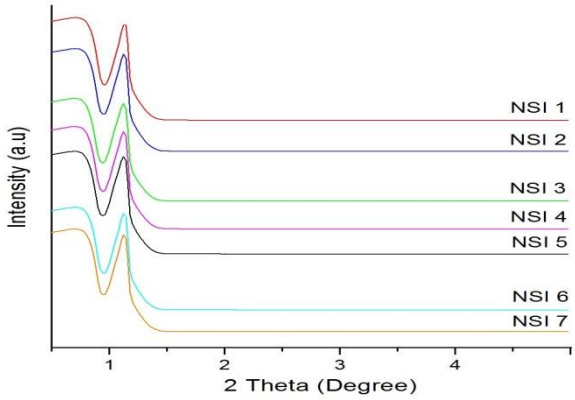

Figure 3. XRD patterns of the gel materials after polymer extraction.

FT-IR spectra of the synthesized samples are shown in Figure 4. The spectra of all samples show the presence of typical silica bands relative to the inorganic framework. The broad band around 1100 cm^{-1}, and at about 463cm^{-1} is due to siloxane (Si-O-Si) groups (Alonso et al. 2004, Berto et al. 2005, Estournes et al. 1997). The frequency bending of the Si–OH band is seen at about 935 cm^{-1} (Estournes et al. 1997, Zhu et al. 2006). The absorption bands at 696 cm^{-1}, 785 cm^{-1} and 1336 cm^{-1} can be assigned to the Si-CH_2 stretching (Gutierrez et al. 2009, Shylesh et al. 2006, Shylesh et al. 2007). Peaks at about 3050 cm^{-1}, 2930 cm^{-1}, 2720 cm^{-1}, 1336 cm^{-1} are due to the vibrations of methylene groups in the APTES precursor (Aridoss et al. 2007, Choi et al. 2012, Kumar et al. 2004, Gutierrez et al. 2009, Nika et al. 2012, Badieia et al. 2011). Stretching vibration of C-N and NH_2 groups is observed at 1230 cm^{-1} and 1510 cm^{-1} respectively (Choi et al. 2012, Palanti et al. 2010). Peaks at 1625

cm^{-1} and 3450 cm^{-1} bands overlapping of O-H, N-H and N-H_2 and groups occurs (Berto et al. 2005, Zhu et al. 2006, Badieia et al. 2011, Denev & Markova 2008, Lee et al. 2011, Bae et al. 2009). These results confirm the successful incorporation of organic and inorganic moiety this means that the synthesized materials are hybrid materials.

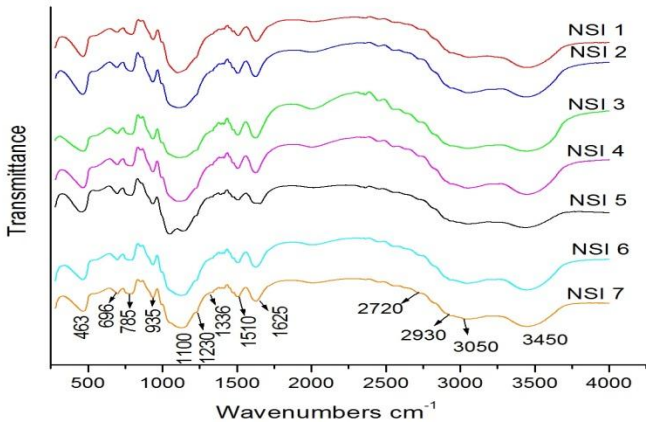

Figure 4. FT-IR spectra of the amine-functionalized materials.

^{13}C CP-MAS NMR spectrums of all samples showed peaks at 10 ppm, 20 ppm and 40 ppm. Figure 5 displays ^{13}C CP-MAS NMR spectrum of NSI 7 sample. The spectra clearly displays three peaks at 10.26, 21.39, and 42.82 ppm, corresponding to the C atoms on the ≡Si-CH_2-CH_2-CH_2-NH_2 group in sequence from left to right (Figure 5) (Wang et al. 2005, Hamoud et al. 2010, Gao et al. 2007, Han et al. 2011, Chong & Zhao 2003, Wang et al. 2005). This confirms FT-IR results that the synthesized materials were indeed functionalized with aminopropyl groups and the organic moiety was not decomposed during the preparation procedure (Zhu et al. 2006). Besides, the lack of peaks in the range of 67-77 ppm that correspond to surfactant P123 implies the complete removal of surfactant P123 during the ethanol extraction (Wang et al. 2005, Chong & Zhao 2003, Wang et al. 2005, Benamor et al. 2012, Yang et al. 2004).

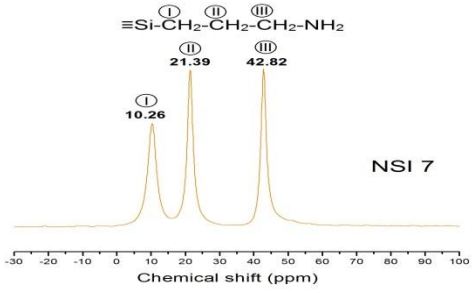

Figure 5. ^{13}C CP-MAS NMR spectrum of NSI 7 sample

The ^{29}Si MAS NMR spectra of all materials (Figure 6) show two distinct resonance peaks corresponding to Q^n (Q^n = $Si(OSi)_n(OH)_{4-n}$, n = 2–4; Q^4 at δ = -112 ppm, and Q^3 at δ = -101 ppm) and two more peaks assigned to T^m (T^m = $RSi(OSi)_m(OH)_{3-m}$, m = 1–3, R is organic group; T^3 at δ = -68

ppm and T^2 at δ = -58 ppm) (Wang et al. 2005). The appearing of Q^3 peak i.e the presence OH group in $(OH)Si(OSi)_3$ means that we have no full condensation in the silicate framework. The inclusion of the organic functional group in the silica framework is confirmed by the appearing of T^m peaks (Wang et al., 2005, Hamoud et al. 2010). The relative integrated intensities of the T^m and Q^n signals in (T^m/Q^n) and $(T^m/(T^m + Q^n))$ were found to increase with increasing of the ratio APTES/(APTES+TEOS) in the initial mixture (Wang et al. 2005, Wang et al. 2005, Wang et al. 2006).

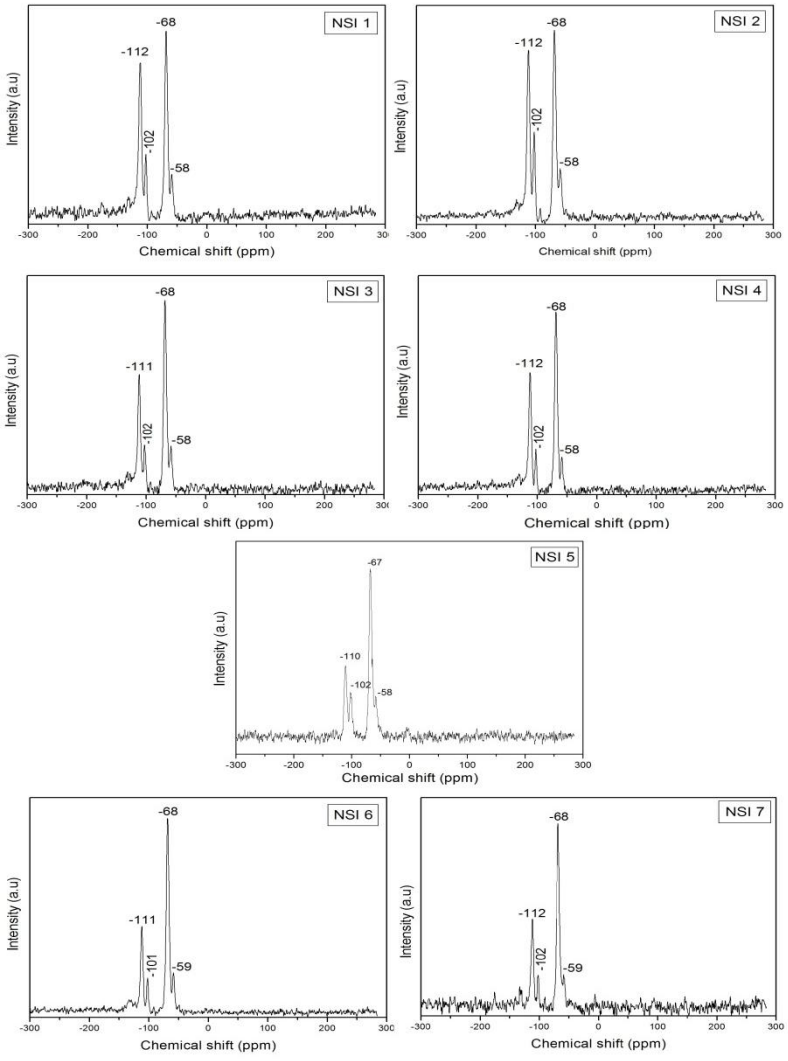

Figure 6. ^{29}Si MAS NMR spectra of the synthesized hybrid gels

The results from elemental analysis are presented in Table2.These results do not show significant differences in the nitrogen amount for the samples synthesized with different acid concentration. These results are in agreement with FT-IR, ^{13}C CP-MAS NMR and ^{29}Si MAS NMR results. The nitrogen amount increase with increasing APTES amount, this confirmed ^{29}Si MAS NMR results presented in Table 3. The results also show that the nitrogen amount in the samples depends only on the APTES amount and that the HCl concentration does not influence on it.

Table 2. Results from the elemental analysis

Sample	Massa mg	C%	H%	N%
NSI 1	1.648	8.41	3.95	4.935
NSI 2	1.302	10.62	4.32	5.4533
NSI 3	1.383	13.84	5.1014	6.6899
NSI 4	1.313	14.27	4.87	6.6044
NSI 5	1.189	13.42	5.24	6.8131
NSI 6	1.475	12.169	5.46	6.9147
NSI 7	1.199	11.69	5.35	6.9087

Table 3. ^{29}Si MAS NMR calculations

Sample	**T^m/Q^n**	**$T^m/(T^m + Q^n)$**	**APTES/(APTES+TEOS)**
NSI 1	1.18	0.54	0.51
NSI 2	1.10	0.52	0.51
NSI 3	1.63	0.61	0.61
NSI 4	1.50	0.59	0.61
NSI 5	2.40	0.70	0.61
NSI 6	2.18	0.68	0.68
NSI 7	1.98	0.66	0.68

SEM images of the synthesized hybrid samples are presented in Figure7. With decreasing the HCl concentration changes occurs in the materials morphology. At the sample prepared with 2M HCl we observe smooth surface, but with decreasing of HCl concentration we observe the obtaining of isolated pores whose size significant increasing to 5µm. As acid concentration increases from 0.18 to2 M, the pore sizes of the hybrid materials decrease, because the protonation of EO at higher acidity may increase the hydrophilic volume and accordingly decrease the hydrophobic PPO core volume of micelles (Qiao et al. 2006, Zhong et al. 2007). In result of the capacity of the PEO block to interpenetrate the inorganic network (obtaining of two-phase model: surfactant-silicate part) which will decrease the pore size. The interpenetration of PEO blocks into the silicate framework leads to a pore model where a low-density 'corona' that is located between the pore center and the silica wall, this less dense zone can be held responsible for the observed microporosity (Soler-Illia et al. 2003, Ryoo & Ko 2000).

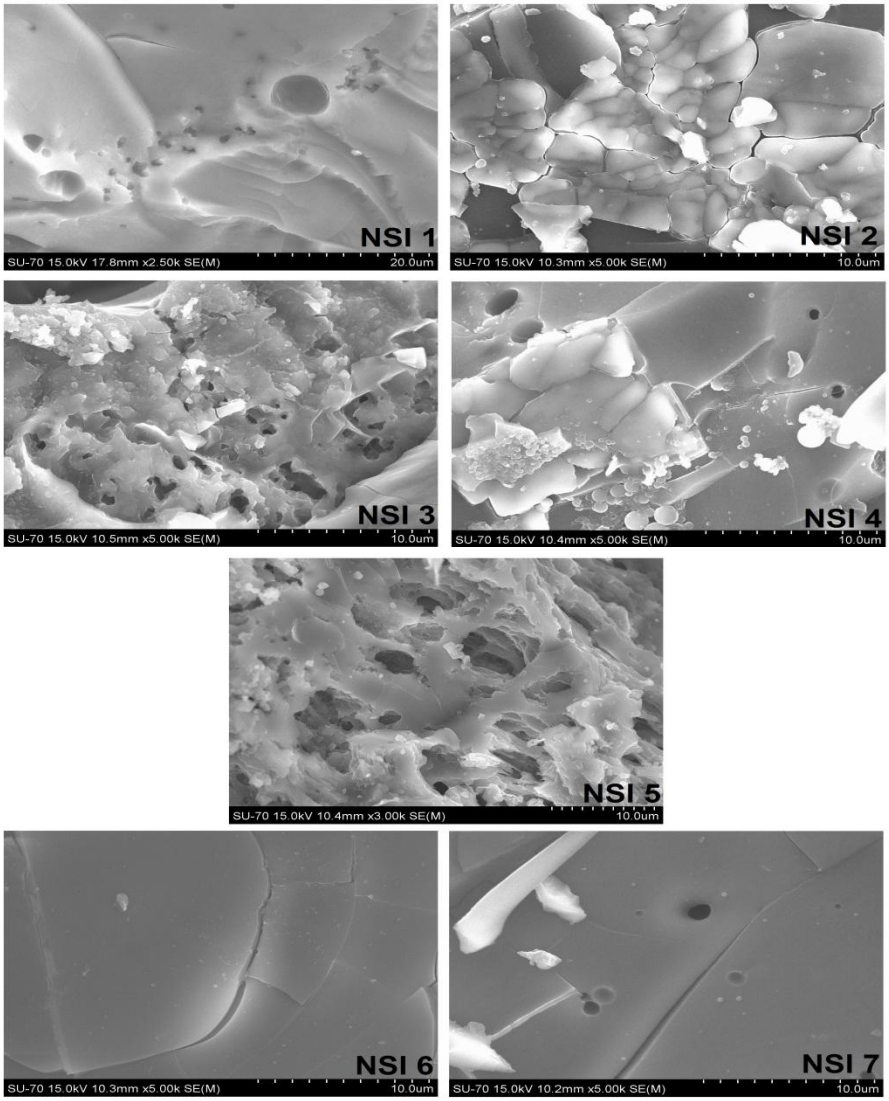

Figure 7. SEM images of thr hybrid gel materials

4. CONCLUSIONS

The above presented results leads to the conclusion that are obtained homogenous hybrid materials synthesized by the co-condensation method of TEOS and APTES using a block copolymer P123 as a structure directing agent. We also can conclude that the acid concentration has not influence on the amount of organic group incorporated in the silica framework. This was confirmed by elemental analysis that does not show difference in the nitrogen amount in the materials. The presence of organic group was confirmed by FT-IR spectra with the appearance of the peaks of methylene groups, Si-CH_2, C-N and NH_2 groups, typical for the APTES precursor. The appearance of T sites in ^{29}Si MAS NMR and the peaks at 10 ppm, 20 ppm and 40 ppm in ^{13}C CP-MAS NMR spectra confirm the presence of organic groups in the silica framework i.e these are organic-inorganic hybrid materials. ^{29}Si MAS NMR spectra showed Q^3 and T^2 type structural units which is indicative of incomplete condensation reactions. The increasing of relative integrated intensities of the T^m and Q^n units suppose that the

amount of organic moiety in the silica wall structures increases with APTES concentration. Besides, no peaks in ^{13}C CP-MAS NMR spectra that correspond to surfactant P123 imply the complete removal of surfactant P123 during the extraction. XRD patterns indicate characteristics of ordered two-dimensional materials (2D) hexagonal structure. Significant difference was observed in SEM images of the samples prepared with different HCl concentration. Increasing of acid concentration lead to decreasing of pore sizes of the hybrid materials in result of increasing the hydrophilic volume and accordingly decreases the hydrophobic PPO core volume of micelles.

ACKNOWLEDGEMENTS

This paper has been produced with the financial assistance of the European Social Fund, project number BG051PO001-3.3.06-0014. The author is responsible for the content of this material, and under no circumstances can be considered as an official position of the European Union and the Ministry of Education and Science of Bulgaria.

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